

The University of Chicago

THE CANNIZZARO REACTION OF AROMATIC ALDEHYDES

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1937

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ALBERT G. CHENICEK

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THE CANNIZZARO REACTION OF AROMATIC ALDEHYDES

The reaction now known as the Cannizzaro reaction was really discovered by Liebig and Wöhler¹ during their study of the action of the hydroxides of the alkali metals on aromatic aldehydes. They stated that, on treatment with concentrated potassium hydroxide, benzaldehyde forms benzoic acid and an "unknown oil." Some years later, this oil was identified as benzyl alcohol by Cannizzaro,² who thus showed that the action of alkali on benzaldehyde results in an intermolecular oxidation-reduction reaction to form the corresponding acid and alcohol.

Since the discovery of Cannizzaro of the disproportionation of benzaldehyde by alkali, a tremendous amount of work has been recorded on the reaction of various substituted aromatic aldehydes with alkali.³ It is well known that many of these aldehydes do not undergo the Cannizzaro reaction, but few attempts have been made to correlate the structure of the aldehyde with the type of reaction it does undergo. We believe that aromatic aldehydes can be divided into three classes according to the type of reaction with alkali:

1. Aldehydes which undergo the Cannizzaro reaction.
2. Aldehydes which evolve hydrogen and form the corresponding acid.
3. Aldehydes which are cloven to the aromatic hydrocarbon and a formate.

Each type of reaction can be associated with the electronegativity of the radical R of the aldehyde RCHO and will be discussed separately.

Aldehydes which undergo the Cannizzaro reaction have a radical R which varies from weakly electronegative to strongly electronegative. There is, however, a distinct variance in ease of disproportionation. The aldehydes with a group R which is

¹Liebig and Wöhler, Ann., 3, 261 (1832).

²Cannizzaro, Ann., 88, 129 (1853).

³For an excellent review see Radovsky, "A Study of the Cannizzaro Reaction" (Unpublished M.S. Thesis, Department of Chemistry, University of Chicago, 1935).

weakly electronegative, react most readily, e.g., the nitrobenzaldehydes react with dilute alkali to form the corresponding acid and alcohol. With concentrated alkali the ortho- derivative gives the azobenzoic acid and the meta- and para- derivatives form the corresponding azoxy compounds.¹ Monohalogen substituted benzaldehydes react less readily than the nitrobenzaldehydes, but faster than benzaldehyde itself. Para-tolulaldehyde reacts more slowly than benzaldehyde and anisaldehyde reacts very slowly.

This variation in ease of reaction can be correlated with the lability of the hydrogen atom attached to the carbonyl group. On this basis, it may be concluded that the more electronegative the group R is, the less readily is the hydrogen atom given up, and the less readily the aldehyde will disproportionate.

Staudinger² has proposed a similar idea in connection with the autoxidation of aldehydes. He studied the relative rates of oxidation of various aromatic aldehydes and concluded that the hydrogen atom is more easily dissociated from benzaldehyde than it is from p-dimethylamino benzaldehyde since benzaldehyde is more easily oxidized. Baeyer and Williger's³ theory of oxidation of aldehydes, and Wieland's⁴ dehydrogenation theory of oxidation, are also based upon the lability of the hydrogen atom of the carbonyl group.

An excellent method of determining the relative labilities of the hydrogen atom of the carbonyl group in different aldehydes is by a mixed Cannizzaro reaction. Thus the aldehyde which is converted to an acid loses its hydrogen atom more readily. Unfortunately there is very little quantitative data available on such reactions. Aromatic alcohols have been prepared by a mixed Cannizzaro reaction of the corresponding aldehyde and formaldehyde, but there is only one publication⁵ reporting the use of two aromatic aldehydes. Reactions were carried out with halogen substituted benzaldehydes and with benzaldehyde or anisaldehyde. In every case the halogen substituted benzaldehyde formed the acid;

¹Maier, Ber., 34, 4132 (1909).

²Staudinger, Ber., 46, 3530 (1913).

³Baeyer and Villiger, Ber., 33, 1569 (1900).

⁴Wieland, Ber., 45, 2606 (1912).

⁵Bailar, Barney, and Miller, J. Am. Chem. Soc., 58, 2110 (1936).

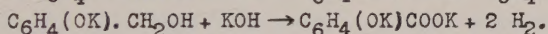
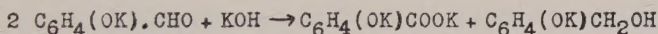
the aldehyde with the less electronegative aromatic radical has the more labile hydrogen atom.

Many investigators have shown that the Cannizzaro reaction is not applicable to all aromatic aldehydes. Thus Piria¹ observed that salicylaldehyde is not converted into salicylic acid except by fusion with alkali. Cannizzaro² later showed that salicylaldehyde does not disproportionate; an observation confirmed by Raikow and Raschtanow.³

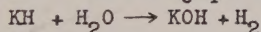
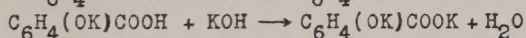
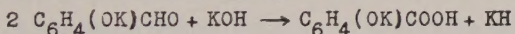
A more thorough study of the reaction with aromatic hydroxy aldehydes was made by Lock.⁴ He found that ortho- and para-hydroxybenzaldehydes give off hydrogen gas when heated with potassium hydroxide at 110° C., while the corresponding alcohols, under similar conditions, liberate hydrogen at about 145° C. With meta-hydroxybenzaldehyde, however, no hydrogen is evolved until a temperature of 190° C. is attained. It was proved that the meta derivative disproportionates even at room temperature and the alcohol formed reacts with the alkali at higher temperatures to give hydrogen.

Lock⁵ advanced two mechanisms to account for the formation of hydrogen in the reaction of an aromatic aldehyde with alkali:

1. For aldehydes undergoing the Cannizzaro reaction, the following mechanism is postulated:



2. Aldehydes which do not undergo the reaction presumably react in the following manner:



Some years earlier, Raikow and Raschtanow⁶ had stated that ortho- and para- substituted hydroxybenzaldehydes do not

¹Piria, Ann., 29, 303 (1839).

²Cannizzaro, Ann., 98, 138 (1856).

³Raikow and Raschtanow, Osterr. Chemiker-Ztg., 5, 169 (1902)

⁴Lock, Ber., 62B, 117 (1929).

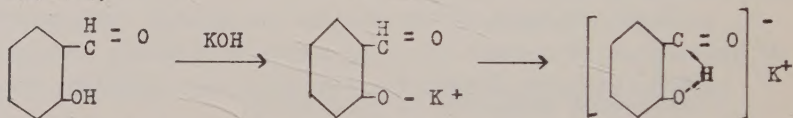
⁵Ibid., 63, 855 (1930).

⁶Op. cit., 169.

disproportionate and correlated this fact with the presence of an hydroxyl group. A similar interpretation was advanced by Lock.¹ The latter investigator called attention to the fact that meta-hydroxybenzaldehyde does undergo the Cannizzaro reaction. Furthermore, he emphasized that a para-hydroxyl group in benzaldehyde still prevents reaction even though a meta-hydroxyl group is present.

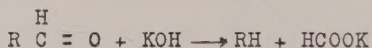
Pauly and Buttlar² ascribed the failure of certain phenolic aldehydes to react to some property of the phenolic oxygen which allowed the formation of a quinoidal compound.

On the assumption that a labile hydrogen atom of the carbonyl group is necessary for the Cannizzaro reaction to take place, an explanation of the failure of some aldehydes to undergo the reaction can be made. The fact that the ortho- and para-hydroxybenzaldehydes do not react is probably best interpreted by assuming hydrogen-bond formation. This would prevent the hydrogen atom of the carbonyl group from entering into the disproportionation reaction.



Since the methyl ethers of the hydroxybenzaldehydes do react, it is necessary to assume that ion formation must take place before the hydrogen bond can form.

Another reaction of concentrated alkali on aromatic aldehydes results in the elimination of the carbonyl group with the formation of a formate and a hydrocarbon.



This cleavage reaction has been carried out with a great variety of substituted benzaldehydes and has been found to be quantitative in many cases. An attempt to correlate the structure of aromatic aldehydes with their susceptibility to cleavage, has been made by Lock.³ He proposed a rule which states that all aldehydes with both ortho positions substituted by chlorine and all derivatives

¹Op. cit., 62B, 1177.

²Pauly and Buttlar, Ann., 383, 216 (1911).

³Lock, Monatsh., 55, 307 (1930).

of meta-hydroxy- and meta-methoxybenzaldehyde in which the two positions ortho to the carbonyl group are occupied by chlorine or bromine atoms, eliminate formic acid when treated with alkali. Later¹ he modified the rule to include aldehydes in which there are two nitro groups in the ortho and para positions. Recent work² showed that benzaldehydes containing a fluorine atom and a chlorine atom, or two fluorine atoms, ortho to the carbonyl group are also included in the class of compounds which are cloven by alkali.

The class of aldehydes which eliminate formic acid on treatment with alkali have a radical R which is very weakly electronegative. The hydrogen atom of the carbonyl group then, is not labile enough for the aldehyde to undergo the Cannizzaro reaction. There is, however, a weaker bond between the carbonyl group and the aromatic nucleus and this is the bond that breaks under more drastic conditions.

The conditions for the elimination of formic acid and for the evolution of hydrogen are much more rigorous than those required for the Cannizzaro reaction. Carbonyl groups of aromatic aldehydes which undergo cleavage are removed by heating the aldehyde, emulsified with 50 per cent potassium hydroxide, on a water bath for one to eight hours. Hydrogen is eliminated only upon fusion of the aldehyde with alkali. There must then be some property of certain aromatic aldehydes which renders them susceptible to the action of alkali and results in disproportionation.

Aldehydes Which Undergo the Cannizzaro Reaction

Benzaldehyde	3-Iodobenzaldehyde
p-Tolualdehyde	4-Iodobenzaldehyde
Anisaldehyde	4-Ethylbenzaldehyde
3-Hydroxybenzaldehyde	4-Phenylbenzaldehyde
2-Nitrobenzaldehyde	2,5-Dimethylbenzaldehyde
3-Nitrobenzaldehyde	2,5-Dichlorobenzaldehyde
4-Nitrobenzaldehyde	2,4-Dichlorobenzaldehyde
2-Chlorobenzaldehyde	3,5-Dichlorobenzaldehyde
3-Chlorobenzaldehyde	3,5-Dimethoxybenzaldehyde
4-Chlorobenzaldehyde	2-Chloro-3-hydroxybenzaldehyde
3-Bromobenzaldehyde	6-Bromo-3-hydroxybenzaldehyde
2-Iodobenzaldehyde	4-Nitro-3-hydroxybenzaldehyde

¹Lock, Ber., 66B, 1759 (1933).

²Ibid., 69B, 2253 (1936).

Aldehydes Which Undergo the Cannizzaro Reaction (Cont'd)

6-Nitro-3-hydroxybenzaldehyde	Isovanillin
2-Iodo-3-hydroxybenzaldehyde	2-Bromoisoanillin
2-Chloro-3-methoxybenzaldehyde	2-Bromoveratraldehyde
4,6-Dibromo-3-hydroxybenzaldehyde	Opiatic acid
4,6-Dibromo-3-methoxybenzaldehyde	Hydrastinin
2-Chloro-4-bromo-3-hydroxybenzaldehyde	Piperonal
2-Chloro-4-bromo-3-methoxybenzaldehyde	Cumaldehyde

Aldehydes Which Eliminate Hydrogen with the
Formation of Corresponding Acid

2-Hydroxybenzaldehyde	5-Methyl-2-hydroxybenzaldehyde
4-Hydroxybenzaldehyde	3-Methyl-2-hydroxybenzaldehyde
3,4-Dihydroxybenzaldehyde	3-Methyl-4-hydroxybenzaldehyde
2,4-Dihydroxybenzaldehyde	β -Naphthol aldehyde
2,4,6-Trihydroxybenzaldehyde	Vanillin
2-Hydroxy-3-methanol-5-methylbenzaldehyde	

Aldehydes Which are Cleaved to Form the Substituted
Aromatic Hydrocarbon and a Formate

2,6-Dibromobenzaldehyde
 2,6-Dichlorobenzaldehyde
 2,3,6-Trichlorobenzaldehyde
 2,4,5,6-Tetrachlorobenzaldehyde
 Pentachlorobenzaldehyde
 2-Iodo-3,6-dichlorobenzaldehyde
 3,6-Dichloro-2-nitrobenzaldehyde
 2,6-Dichloro-3-nitrobenzaldehyde
 3-Methoxy-2,6-dinitrobenzaldehyde
 3-Methoxy-4,6-dinitrobenzaldehyde
 2,6-Dichloro-3-hydroxybenzaldehyde
 2,6-Dichloro-3-methoxybenzaldehyde
 2,4,6-Trichloro-3-methoxybenzaldehyde
 2,4,6-Tribromobenzaldehyde
 2,4,6-Tribromo-3-methoxybenzaldehyde
 2-Chloro-4,6-dibromo-3-hydroxybenzaldehyde
 2-Chloro-4,6-dibromo-3-methoxybenzaldehyde
 4-Bromo-2,6-dichloro-3-hydroxybenzaldehyde
 4-Bromo-2,6-dichloro-3-methoxybenzaldehyde
 2,4,5,6-Tetrachloro-3-methoxybenzaldehyde

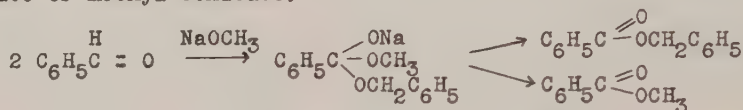
Aldehydes Which are Cloven to Form the Substituted
Aromatic Hydrocarbon and a Formate (Cont'd)

2-Chloro-6-bromo-3-hydroxybenzaldehyde
2,4-Dichloro-6-bromo-3-hydroxybenzaldehyde
4,6-Dibromo-2-iodo-3-hydroxybenzaldehyde
2,6-Dibromo-3,5-dimethoxybenzaldehyde
2,6-Dichloro-3,5-dimethoxybenzaldehyde
2-Bromo-3,5-dimethoxybenzaldehyde
2-Chloro-3,5-dimethoxybenzaldehyde
2-Chloro-6-fluorobenzaldehyde¹
2,6-Difluorobenzaldehyde
2,6-Dibromoveratraldehyde
2-Nitro-6-bromoveratraldehyde
2,6-Dinitroisovanillin

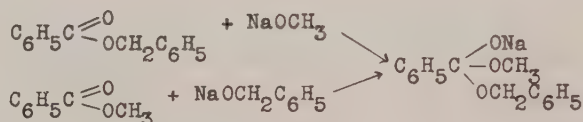
¹Some Cannizzaro reaction.

PROPOSED MECHANISMS FOR THE CANNIZZARO REACTION

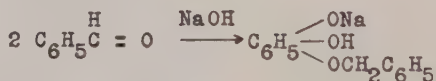
Numerous reaction mechanisms have been proposed for the Cannizzaro reaction to explain the known facts. One of the earliest mechanisms, although not strictly for the Cannizzaro reaction, was proposed by Claisen.¹ He determined the action of sodium methylate on benzaldehyde and isolated benzyl benzoate and methyl benzoate besides some benzoic acid and benzyl alcohol. To account for these products, he assumed the formation of an intermediate ortho ester which could decompose in two ways: to form benzyl benzoate or methyl benzoate.



This same ortho compound could be formed by the action of sodium methylate on benzyl benzoate, or of sodium benzylate on methyl benzoate.



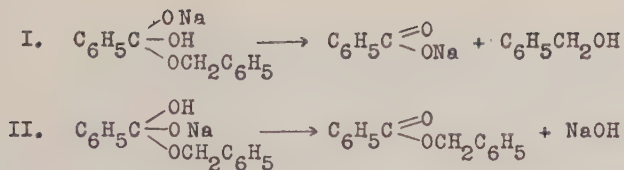
Kohn and Tranton² later observed that in the absence of water or in the presence of an excess of benzaldehyde, benzyl benzoate was the main product of the action of sodium hydroxide on benzaldehyde. They proposed the formation of an intermediate similar to that of Claisen.



In the presence of water, hydrolysis takes place to form benzyl alcohol and sodium benzoate. In the absence of water two reactions are possible:

¹Claisen, Ber., 20, 646 (1887).

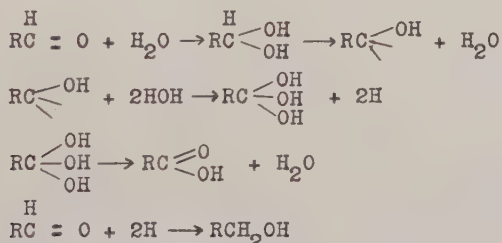
²Kohn and Tranton, J. Chem. Soc., 75, 1155 (1899).



These are identical with Claisen's explanation of the formation of two possible esters. The first decomposition is assumed to take place more readily than the second and is favored by an excess of alkali. An excess of aldehyde favors the second reaction.

Tischenko¹ also proposed a mechanism which is practically the same as that of Kohn and Tranton. In the absence of water, the ester is formed; in the presence of water the ester is saponified to the acid salt and the alcohol.

A mechanism based on his theory of the divalent carbon atom has been published by Nef.² An aldehyde hydrate is assumed to be necessary as shown in the following representation of the reaction.



Wieland's³ mechanism is based upon his theory of enzyme catalysis. He states that the hydrogen atom of the aldehyde group is activated and another molecule of aldehyde acts as an acceptor, resulting in the disproportionation of the aldehyde. This is essentially the idea discussed in the introductory part of this work.

Meerwein⁴ and Lachmann⁵ have also proposed mechanisms for the Cannizzaro reaction, the latter's involving a reaction similar

¹Tischenko, J. prakt. Chem., **86**, 322 (1862).

²Nef, Ann., **298**, 202, 301 (1897).

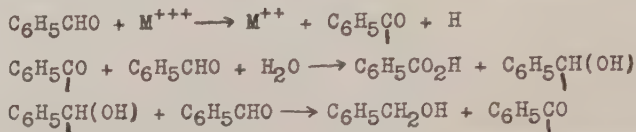
³Wieland, Ber., **45**, 2606 (1912).

⁴Meerwein, Ann., **444**, 221 (1925).

⁵Lachmann, J. Am. Chem. Soc., **45**, 2356 (1923).

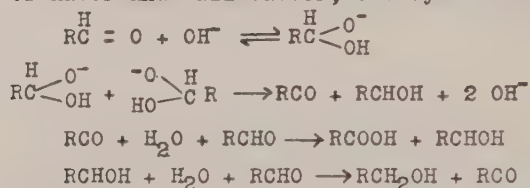
to the pinacol rearrangement.

The theory of the autoxidation of benzaldehyde proposed by Haber and Willstätter, which was derived from their generalization of enzyme catalysis, is the basis for their mechanism of the Cannizzaro reaction.¹ Trivalent metals such as iron, are catalysts for the autoxidation of benzaldehyde and thus Haber and Willstätter assume these metals are also catalysts for the Cannizzaro reaction. The mechanism which they present is as follows:



The trivalent metal acts as a catalyst through the initiation of a chain reaction.

One other mechanism which is also a chain reaction has been published.² Geib has proposed the formation of the same two radicals of Haber and Willstätter, but by a different process.



On the basis of his studies of the Cannizzaro reaction, Geib draws the following conclusions:

1. In the heterogeneous reaction, primary and secondary (but not tertiary) alcohols as well as metal hydroxides, affect the reaction.
2. No inhibitor of the heterogeneous reaction was found.
3. The velocity of the reaction is the same for sodium hydroxide and potassium hydroxide.
4. In 60 per cent ethyl alcohol solution, the reaction velocity is one-fifth of that in water.
5. The homogeneous reaction cannot be catalyzed.
6. The collision between two molecules of the addition product of hydroxyl ion and aldehyde is considered essential to the occurrence of the reaction.

¹Haber and Willstätter, Ber., 64B, 2844-56 (1931).

²Geib, Z. physik. Chem., A169, 41-51 (1934).

THE CANNIZZARO REACTION OF BENZALDEHYDE

Preliminary work on the Cannizzaro reaction of anisaldehyde, p-tolualdehyde, and benzaldehyde¹ showed that, in general, commercial aldehyde taken directly from its original container and aldehyde which had been distilled in the absence of air reacted at different rates, distilled aldehyde having the lower rate.² It was also shown that the rate might be affected by the addition of various foreign substances. This clearly indicated a catalytic effect of some nature which, from the results of this preliminary work, was postulated to be due to peroxides in the aldehyde. These peroxides are present in commercial aldehyde and are removed by distillation in the absence of air.

It was the purpose of the present work to make a study of the conditions affecting the rate of reaction of one aldehyde and to determine, if possible, the exact nature of the catalyst responsible for variations in rate of reaction under identical experimental conditions.

Benzaldehyde³ was chosen for this investigation because of its comparatively rapid reaction and its well known sensitivity towards oxygen.

Experiments were first carried out to determine how variations in reaction conditions effected the rate of reaction.

¹Kharasch and Foy, *J. Am. Chem. Soc.*, 57, 1510 (1935); Foy, "Cannizzaro Reaction of Aldehydes as a Function of Peroxide Content" (Unpublished Ph.D. Dissertation, Department of Chemistry, University of Chicago, 1936).

²The word "rate" is used in this thesis to represent the per cent Cannizzaro reaction in a given time. Thus when one reaction is said to have a greater rate than another it is meant that the two reactions were carried out under identical conditions at the same time, the reaction giving the greater per cent disproportionation having the greater rate.

³The benzaldehyde used throughout this work was F. F. C. quality obtained from Van Ameringen-Haebler, Inc. in one-pound brown bottles. Because of the unexplained variation in the rate of Cannizzaro reaction with time of standing of either untreated or distilled aldehyde it was necessary to run control experiments in each instance in order to determine the effect of any treatment or added substance on the rate of the reaction.

Different brands of potassium hydroxide were tried, reagent grade, C.P., and U.S.P. quality. If the concentrations, as determined by titration, were made identical the source of the alkali had no effect upon the rate of the Cannizzaro reaction. There also was no difference between the action of a solution of the alkali in ordinary distilled water and conductivity water.

Changes in the concentration of the alkali, of course, affected the rate of reaction. The results of such a variation are tabulated in Table 1.

TABLE 1
EFFECT OF CONCENTRATION OF POTASSIUM HYDROXIDE

Conc. KOH	moles ald./moles KOH	Per Cent Reaction ^b		
		Untreated ald.	Dist. ald.	
40% ^a	0.979	14	17	
46	0.782	19	14	11
50	0.702	68	39	15
56.5	0.603	55	55	

^aPer cent by weight.

^b40 C., time one-half hour.

In a series of reactions with different concentrations of alkali, the ratio of the aldehyde concentration to the alkali concentration was kept constant by changing the volume of each and keeping the total volume constant. The following results were obtained.

TABLE 2
EFFECT OF CONCENTRATION OF POTASSIUM HYDROXIDE
AT CONSTANT PROPORTION OF ALDEHYDE

moles ald./moles KOH	Conc. KOH	Per Cent Reaction
1	40%	18
	46	20
	50	33
	56.5	45

The effect of the volume of the potassium hydroxide solution was also determined, the number of moles of alkali being doubled.

TABLE 3

EFFECT OF VOLUME OF KOH SOLUTION

Solution	Per Cent
5.0 cc. 50% KOH and 5.0 cc. ald.	26
5.0 cc. 50% KOH, 5.0 cc. ald. and 5.0 cc. benzene	14
10.0 cc. 50% KOH and 5.0 cc. ald.	37

The temperature at which the reaction is carried out is also of importance. Three different temperatures were used and the amount of reaction after one hour determined.

TABLE 4

VARIATION OF REACTION RATE WITH TEMPERATURE

Temperature	Per Cent Reaction	
	Untreated aldehyde	Distilled aldehyde
40° C.		19
25	26	15
0	6	11

With untreated aldehyde, the volume of the reaction tube had a very decided effect upon the rate of reaction as shown in the following table.

TABLE 5

EFFECT OF VOLUME OF REACTION TUBE ON RATE OF REACTION

Volume of Tube	Per Cent Reaction	
	Untreated aldehyde	Distilled aldehyde
40 cc.	83	26
18 cc.	29	20

The reason for this difference will be discussed later.

After this preliminary survey of reaction variables, the following conditions were adopted as standard and used for all reactions unless otherwise noted. Pyrex glass reaction tubes, to which a neck of six millimeter tubing was sealed, were used. The total volume was 18 cubic centimeters. Five cubic centimeters

(0.07 moles) of 50 per cent potassium hydroxide and five cubic centimeters (0.05 moles) of benzaldehyde were pipetted into the tube which was then sealed off. These tubes were fastened radially to a rotating disk in a thermostat maintained at $25.0 \pm 0.1^\circ \text{C.}$, and rotated slowly for one hour. At the end of this time, the tubes were removed and immediately cooled in a carbon dioxide-acetone mixture to stop the reaction.

These first experiments to fix conditions for a study of the Cannizzaro reaction, showed that distilled benzaldehyde and benzaldehyde taken directly from a bottle, reacted at different rates under the same conditions. It was then desirable to study the reaction of these two aldehydes and determine the cause of the difference between them.

When the Cannizzaro reaction was carried out with benzaldehyde from a bottle which had just been opened, the rate of reaction was slow and there was no difference in rate between a reaction which took place in a tube containing air and in a tube which had been evacuated. Upon standing, however, a difference in rates developed; the reaction in air greatly increased in rate while the rate of reaction in an evacuated tube was only slightly altered. This difference was not due to an emulsifying effect due to the air, because the rate was the same in a tube containing nitrogen as in an evacuated tube. It was found that the time of standing before an air-vacuum difference¹ appeared, varied with different bottles of aldehyde. An important fact in this connection is, that the longer the time necessary to produce the difference the smaller the increase in rate.

If the aldehyde which had developed an air-vacuum difference was allowed to stand in a stoppered bottle for a few months, the rate of reaction fell to that of the aldehyde when the bottle was first opened and the air-vacuum difference disappeared. Upon opening the bottle again, a difference did appear, but it was not as large as before nor did it last as long as it had previously. From the time of the second decrease in rate, the air-vacuum difference could not be made to reappear even after long standing of the aldehyde exposed to air. Later, benzaldehyde from four more bottles was used to check this effect of aging. In no case did an air-vacuum difference develop (see Table 6 for aging of aldehyde from the bottle). An air-vacuum difference was observed with aldehyde from bottles other than those listed in the table but no aging effect was studied.

¹"vacuum" when used in the term "air-vacuum difference," means reduced pressure (evacuated with an oil pump).

TABLE 6

AGING OF UNTREATED ALDEHYDE

Bottle Number	Days of Standing	Per Cent Reaction	
		Air	Vacuum
7	41	56	34
	56	61	55
	62	44	30
11	4	19	17
	7	70	39
	12	68	
	19	72	
	25	73	35
	36	67	35
	131	27	24
	131*	47	50
	132	38	50
	133	33	39
	133	31	39
	168	54	20
	204	26	23
	210	28	29
	249	26	28
	289	30	28
12	20	37	28
	26	33	27
	33	36	35
	35	31	
	39	34	36
	47	49	31
	126	54	
15	173	28	17
	0	18	12
	3	14	15
	9	20	22
16	53	23	23
	0	15	15
	14	21	15
	32	18	19
17	48	20	26
	0	17	14
	14	17	16
	30	18	23
18	47	19	18
	0	13	16
	14	19	15
	23	24	14
	30	21	18
	47	19	17

*Run made three hours later.

The results obtained with aging indicate that some substance is formed in some samples of benzaldehyde by the action of air, either on the aldehyde itself or on some impurity in the aldehyde. This substance catalyzes the Cannizzaro reaction of the aldehyde only if air (oxygen) is present in the reaction tube. A peroxide of the aldehyde would be the most likely substance formed in addition to benzoic acid, but if a peroxide is the catalyst, all samples of aldehyde should act similarly and it should be possible to make the air-vacuum difference reappear upon exposure of the aldehyde to air. Since this is not possible, the catalyst is probably some substance other than an aldehyde peroxide, which is present in the aldehyde as an impurity. The benzaldehyde used was free from added antioxidants, thus the most likely impurities would be benzoic acid and benzyl alcohol. If the alcohol is the catalyst, induced oxidation by aldehyde peroxides would finally convert all of it into aldehyde or acid and its catalytic influence would disappear. This would account for the effect of aging, since an air-vacuum difference would presumably reappear as long as some alcohol was present.

When benzaldehyde is distilled, in the absence of light, at reduced pressure in an atmosphere of carbon dioxide or in high vacuum, the rate of the Cannizzaro reaction of the aldehyde is decreased, and there is no air-vacuum difference. The rate of reaction is about the same no matter what the rate of the original aldehyde used for the distillation. There also is always a slight increase in rate of reaction of aldehyde which has been standing in air a few days over the rate of aldehyde which is freshly distilled. In neither case is an air-vacuum difference detectable. Standing for long periods of time does not produce such a difference (see Table 7 for aging of distilled aldehyde).

The slower rate of reaction of benzaldehyde after distillation shows that the substance responsible for the air-vacuum difference is removed by distillation either because it is higher or lower boiling than the aldehyde itself, is non-volatile, or is decomposed by heat. Experiments were made to determine which of these factors is responsible for purification. Reactions were carried out with the first fraction, ordinarily discarded, which would contain all the low boiling compounds; on the middle fraction which was ordinarily used; and on the residue. If a small amount of some residues was added to distilled aldehyde, it increased the

TABLE 7
AGING OF DISTILLED ALDEHYDE

Aldehyde Sample No.	Method of Purification	Days of Standing	Per Cent Reaction	
			Air	Vacuum
III	Bisulfite ald. decomp. with sulfuric acid, washed with sodium carbonate soln. and distilled at reduced pressure under CO ₂	0	28	33
		2	44	32
		7	42	33
		14	68	51
		19	81	64
IV	Washed with sodium sulfite and sodium carbonate solutions, distilled at reduced pressure under CO ₂	0	20	26
		7	37	32
		12	36	33
		15	35	
		33	28	
V	Washed and distilled as aldehyde IV	0	25	23
		3	30	25
		9	27	26
X	Distilled at reduced pressure under CO ₂	0	26	
		1		17
		4	13	17
		10	28	31
		58	25	26
XI	Distilled at reduced pressure under CO ₂	0	16	
		1		12
		5	34	
		50	25	23
XV	Distilled in high vacuum	0	15	12
		3	18	16
		0	17	17
XVIII	Distilled in high vacuum	0	20	
		4	28	
		10	26	24
		11	15	

rate of the Cannizzaro reaction; with other fractions there was no effect. The first and middle fractions of the aldehyde reacted at the same rate. These results indicate that the active component of aldehyde from the bottle is removed by heating either through polymerization or actual decomposition. One reaction was carried out with aldehyde which had been heated at 80-90° C. in an evacuated tube for one-half hour. The heated aldehyde reacted slightly less than plain aldehyde (52 per cent and 64 per cent respectively).

The bottles which showed an air-vacuum difference had been standing on a shelf where they were exposed to direct sunlight during the summer months. The last four bottles (15-18) which showed no air-vacuum difference, were allowed to stand in the same place, but the period was during the winter. Thus it is possible that the greater light intensity or higher temperature, or both, during the summer may account for the difference between the two sets of bottles.

There is one other difference between the aldehydes, namely, that crystals of benzoic acid appeared on the walls of the bottles that were kept on the shelf containing aldehyde which did not show an air-vacuum difference. No crystals appeared in those bottles of aldehyde which did show such a difference until that difference had disappeared. No benzoic acid crystals appeared if the bottles were kept in the dark.

Since the crystals of benzoic acid on the walls of certain bottles of aldehyde seemed to be formed by the action of light, and no crystals formed in bottles of aldehyde which showed an air-vacuum difference, a trace of water (1 per cent which dissolved completely) was added to distilled aldehyde. Water is known to inhibit the action of light on benzaldehyde and it was hoped that the addition of a small amount of water would produce an air-vacuum difference. The aging of this aldehyde was followed.

TABLE 8
AGING EFFECT OF DISTILLED ALDEHYDE
CONTAINING 1 PER CENT WATER

Days of Standing	Per Cent Reaction	
	Air	Vacuum
0	22	17
5	20	19
30	25	27

As expected, the addition of water prevented the formation of crystals of benzoic acid on the walls of the bottle. However, no air-vacuum difference was observed.

Here was evidence that another factor, namely light, might affect the rate of the Cannizzaro reaction. From all the foregoing facts, one can conclude that the substance responsible for the difference in rate of the Cannizzaro reaction when allowed to take place in the presence and absence of air, is not benzoic acid, benzyl alcohol, or aldehyde peroxides, but probably an active molecule or a free radical. If this is true, the active component would exist only in solution in the aldehyde and could not be isolated. Light does produce activated molecules and free radicals, especially from carbonyl compounds and could be used to produce these substances in a solution of benzaldehyde.

Preliminary experiments on the effect of light on the Cannizzaro reaction, were made by exposing distilled benzaldehyde, in pyrex glass tubes, to direct sunlight. The alkali was then added and the tubes sealed off as before. It was found that the rate of reaction was greatly increased after exposure of one hour.

In order to obtain standard conditions, experiments were carried out using a quartz mercury arc as a source of illumination. These experiments were to determine the time of exposure and the distance from the lamp necessary to produce a fairly large increase in rate. With the tubes in a rack rotating about the lamp three and one-half inches away, exposure for one hour was found to give good results. The amperage used for the lamp was kept constant. Thus with conditions fixed, the results of all reactions using illuminated aldehyde should be comparable.

In an attempt to produce an air-vacuum difference, a large quantity of distilled aldehyde was illuminated for one hour and stored in a brown bottle. The aging of this aldehyde was followed.

TABLE 9
EFFECT OF AGING OF ILLUMINATED DISTILLED ALDEHYDE
STORED IN BROWN BOTTLE

Days of Standing	Per Cent Reaction	
	Air	Vacuum
0	56	46
10	21	19
14	24	32
22	23	21
64	26	28

This illuminated aldehyde showed a definite aging effect but no air-vacuum difference.

When distilled benzaldehyde is exposed either to sunlight or to the light of a mercury arc for a period long enough to double the rate of the Cannizzaro reaction of unexposed aldehyde, a noticeable yellow color appears. This color becomes lighter if the aldehyde is allowed to stand in air, but increases in intensity when the aldehyde is allowed to stand in an evacuated tube. The color can be made to disappear by shaking the aldehyde in air, which is considered as evidence that the yellow color may be due to free radicals and its disappearance to the formation of colorless peroxides. Too long an exposure to light causes the formation of a permanent yellow color which is probably due to the formation of polymers.

Evidently there is some reaction between illuminated benzaldehyde and oxygen which might be responsible for the increased rate of the Cannizzaro reaction of illuminated aldehyde. Benzaldehyde, therefore, was exposed to light in the presence and absence of air, and then allowed to undergo the Cannizzaro reaction. It was found that aldehyde illuminated in air and shaken in air before the alkali is added, reacted much faster than aldehyde which had not been illuminated. When the aldehyde is illuminated in vacuo and shaken in air before adding alkali, the rate of reaction is also increased. On the other hand, if aldehyde is illuminated in vacuo and well cooled before the tube is opened to add the alkali, there is no increase in rate of the Cannizzaro reaction. Illuminated aldehyde in tubes both open to the air and evacuated, was allowed to stand in the dark and then used in the Cannizzaro reaction. A summary of the results obtained with illuminated aldehyde is given in Table 10. This shows quite definitely that the peroxides catalyze the reaction.

When benzaldehyde was exposed to sunlight for a few months, a white crystalline solid separated. This was isolated and identified as the tetramer of benzaldehyde. It had, however, no effect upon the rate of the Cannizzaro reaction.

Other experiments on the effect of light were carried out. Benzaldehyde containing a trace of water was illuminated and the rate of the Cannizzaro reaction compared with that of aldehyde containing no water. The rate was slightly lower than that of illuminated benzaldehyde.

TABLE 10

EFFECT OF AGING ON ILLUMINATED DISTILLED ALDEHYDE

Illumination in Air	Treatment after Illumination (Shaken in Air)	Time of Standing (hours)	Per Cent Reaction	
			Illuminated	Not Illuminated
Yes	Yes	0	53	16
Yes	Yes	72	51	16
No	Yes	0	48	16
No	Yes	72	50	16
No	Yes	0	40	8.0
No	No	190	15	8.0
No	No	0	24	22
No	Yes	0	28	16
No	Yes	72	35	16
No	No	0	20	20
No	No	72	13	15
Yes	Yes	0	33	16
Yes	Yes	72	36	16
Yes	Yes	0	30	15
Yes	No	0	17	15

A small quantity of β -naphthol was added to distilled benzaldehyde and the solution illuminated with ultraviolet light for one hour. The rate of reaction was increased over that of plain illuminated aldehyde.

TABLE 11

EFFECT OF ADDED SUBSTANCES ON ILLUMINATED
DISTILLED ALDEHYDE

Substance Added	Per Cent Reaction with Substance	Per Cent Reaction plain illum.
1/5000 pts. β -naphthol	50	31
1/5000 pts. β -naphthol added after illumina- tion	43	31
0.4% water	31	45

When benzaldehyde in containers of brown glass is illuminated, the light has no effect upon the rate of the Cannizzaro reaction. The effective wave lengths were absorbed by the glass.

Experiments were also made using an incandescent lamp as a source of light. A two hundred watt lamp had no effect even after exposure for three hours at a distance of one inch.

Other reagents were sought which might have an action similar to that of light. The effect of condensing agents was tried in order to determine whether or not active fragments were formed by their action on benzaldehyde.

When sulfuric acid is added to benzaldehyde, a yellow color immediately appears which changes to a red color upon standing. The rate of the Cannizzaro reaction using aldehyde containing a small quantity of sulfuric acid is greatly increased over that of distilled aldehyde. There is, however, no air-vacuum difference.

Attempts were made to isolate some substance from reaction mixtures of concentrated sulfuric acid and benzaldehyde. Two different solids were isolated (see Experimental Part), but neither one increased the rate of reaction when added to distilled aldehyde.

Phosphorus pentoxide was also added to benzaldehyde and the mixture treated to remove all excess aldehyde. The residue was a dark brown gum which, when a portion of it was added to distilled aldehyde, increased the rate of the Cannizzaro reaction. Again there was no air-vacuum difference.

It is known that when dry hydrogen chloride gas is passed into benzaldehyde a red color is imparted to it. Since the presence of sulfuric acid in benzaldehyde also produces a red color along with an increase in rate of the Cannizzaro reaction, a solution of hydrogen chloride in benzaldehyde was tried. The acid reacted immediately with the alkali and potassium chloride separated. When a drop of a hydrogen chloride solution was added to distilled aldehyde, there was no effect upon the rate of reaction.

Phosphoric acid was also added to benzaldehyde and its effect on the rate of reaction determined. There was no increase in rate over that of plain benzaldehyde.

The results of the addition of these various compounds to distilled aldehyde are summarized in Table 12.

TABLE 12

EFFECT OF ADDED SUBSTANCES ON RATE OF REACTION

Substance Added	Per Cent Reaction		Per Cent Reaction Nothing Added	
	Air	Vacuum	Air	Vacuum
0.4% H_2SO_4 (yellow ald.)	87	72	33	23
0.4% H_2SO_4 (red ald.)	91	90	33	23
1/5000 pts. polymer from H_2SO_4	25	27	35	26
phosphorus pentoxide residue	77		31	
HCl in benzaldehyde	24		31	
0.2 cc. 85% phosphoric acid	30		25	

The possibility of benzyl alcohol as the catalyst of the Cannizzaro reaction had been considered before, but no extensive experiments to determine the effect of this reagent were made. Since, however, the more likely possibilities did not produce the sought-for air-vacuum difference, the effect of benzyl alcohol was studied in greater detail.

When ordinary benzyl alcohol is added to aldehyde from the bottle, the rate of the Cannizzaro reaction is increased, the amount depending upon the quantity of alcohol used. Later work showed that benzyl alcohol, added to a reaction using aldehyde which showed an air-vacuum difference, increases the rate of reaction in air but has no effect upon the rate in vacuo. Thus the addition of benzyl alcohol increases the air-vacuum difference when the reaction already exhibits such an effect.

When ordinary benzyl alcohol is added to distilled aldehyde and the solution used in the Cannizzaro reaction, the rate is increased. This alcohol contains a large quantity of peroxides. Peroxide-free benzyl alcohol was prepared and used to determine if the peroxides of the alcohol were responsible for the increase in rate. Reactions were carried out with peroxide-free and peroxide-containing benzyl alcohol. The results are tabulated in Table 13.

Both peroxide-containing and peroxide-free benzyl alcohol catalyze the Cannizzaro reaction of benzaldehyde. It must be remembered, however, that the aldehyde itself is not peroxide-free,

and might produce peroxides in the alcohol. No air-vacuum difference is detectable.

TABLE 13
EFFECT OF BENZYL ALCOHOL ON RATE OF REACTION

Amount and Kind of Alcohol	Per Cent Reaction with Alcohol		Per Cent Reaction Nothing Added	
	Air	Vacuum	Air	Vacuum
1% peroxide-containing	59	56	14	13
1% peroxide-free	20	36	14	13
0.1% peroxide-containing	17		22	
0.1% peroxide-free	25		22	
1% peroxide-containing	27		10	
1% peroxide-free	26		10	
1% peroxide-containing	40		15	
1% peroxide-free	45		15	

The aging of distilled aldehyde containing benzyl alcohol was also studied. The result show that the alcohol was used up in some way, probably by oxidation, as had been predicted.

TABLE 14
AGING EFFECT ON BENZALDEHYDE CONTAINING BENZYL ALCOHOL

Amount of Alcohol	Days of Standing	Per Cent Reaction	
		Air	Vacuum
1%	0	46	46
	3	44	28
	9	34	31
	22	38	30
	59	29	22
0.5%	0	34	33
	15	28	22

The effect of benzyl benzoate was also tried. It has no

effect upon the rate of reaction even though it saponifies very readily. One per cent of the ester was added to distilled aldehyde and the solution allowed to stand. The results of aging are given in the following table.

TABLE 15
EFFECT OF BENZYL BENZOATE ON RATE OF REACTION

Days of Standing	Per Cent Reaction	
	Air	Vacuum
0	19	16
6	17	20
29	21	20

There was the possibility that the acid present in the aldehyde decreases the alkali concentration and thus reduces the rate of reaction. It was found that the addition of benzoic acid or sodium benzoate to the reaction mixture, has no effect upon the extent of reaction. In one case the amount of acid in the aldehyde was titrated and sufficient excess alkali added to just neutralize the acid. Another reaction was carried out without the excess alkali; both reacted to the same extent.

Reaction tubes containing distilled aldehyde and the alkali were filled with oxygen and sealed off. A comparison of rates was made with reactions carried out in evacuated tubes. There was no difference. Even if oxygen was bubbled through the aldehyde before the alkali was added, no increase in rate was observed. Reactions were also made, in the presence of oxygen, with the addition of small amounts of ferric chloride. This did not increase the rate.

The total peroxide content of various samples of benzaldehyde was titrated before the reactions were started. It was found that the peroxide content and extent of reaction cannot be correlated. Data are listed in Table 16.

This lack of correlation does not exclude the possibility of a single peroxide being a catalyst, since only the total peroxide content was titrated and any one peroxide could be present in varying amounts. To find if a certain peroxide was responsible for the increase in rate of the Cannizzaro reaction carried out

in air over that of a reaction in an evacuated tube, peroxides of benzaldehyde were prepared and their effect with distilled aldehyde determined. (One peroxide, dibenzal-dihydro-peroxide was not prepared.) None of the peroxides tried had any effect upon the rate of the Cannizzaro reaction.

TABLE 16
VARIATION OF RATE OF REACTION WITH PEROXIDE
CONTENT OF BENZALDEHYDE

Aldehyde	Peroxide Content	Per Cent Reaction	
		Air	Vacuum
7	0.00166 N	56	34
7	0.00320 N	61	55
11	0.00223 N	70	39
11	0.00893 N	37	28
12	0.00271 N	28	23
12	0.00283 N	37	28
12	0.00186 N	31	
I	0.00169 N	30	32
II	0.0044 N	44	
II	0.00338 N	65	63
III	0.00117 N	28	33
III	0.00295 N	44	32
III	0.0023 N	68	51
III	0.00231 N	81	

Although these relatively stable peroxides did not affect the rate of reaction, a primary peroxide or moloxide, might affect it. The presence of such a peroxide in benzaldehyde has been proposed by others because the aldehyde, upon exposure to air, has a greater oxidizing power than have the other known peroxides.

When the peroxide content of distilled aldehyde was titrated, it was difficult to obtain a good end-point. This was because of the rapidity of peroxidation even though attempts were made to keep an atmosphere of carbon dioxide above the solution. The end-point changed only slowly when aldehyde from the bottle was used. This is good evidence that even active peroxides do not affect the rate of the Cannizzaro reaction, since distilled aldehyde reacts more slowly than bottled aldehyde even in the presence of iron. (The iron present in the titrating solution is presumably a catalyst for the oxidation of the benzaldehyde during the titration.)

Various inorganic compounds were added to reaction mixtures, using both aldehyde from the bottle and distilled aldehyde, which might conceivably be present in the aldehyde or alkali as impurities. Other substances were tried which are catalysts or inhibitors of the autoxidation of benzaldehyde. Table 17 contains all these inorganic compounds except those discussed previously.

TABLE 17
EFFECT OF ADDED INORGANIC SUBSTANCES ON
UNTREATED ALDEHYDE

Substance Added	Per Cent Reaction		Per Cent Reaction Nothing Added	
	Air	Vacuum	Air	Vacuum
0.1 gr. potassium cyanide	30		73	
0.01 gr. palladium oxide	66		73	
0.1 gr. cuprous chloride	100		80	
1/10,000 parts cuprous chloride	62	43	34	36
0.05 gr. ammonium hydroxide solution	47		80	
0.1 gr. ferrous sulfate	50		91	44
0.2 gr. ferrous sulfate	33		72	
0.3 gr. sodium sulfite	1.5?		15	
0.3 gr. sodium sulfide	1.3?		15	
1/10,000 parts manganese chloride	53	28	49	31
Trace iodine	30	33	49	31
0.1 gr. potassium chloride	68		65	
0.1 gr. potassium carbonate	90		81	
0.1 gr. barium chloride	84		81	

Ferrous sulfate and manganese chloride, which greatly accelerate the autoxidation (peroxidation) of benzaldehyde, are not catalysts for the reaction. Ferrous sulfate, in fact, decreases the rate of reaction in air. The other compounds which decrease the rate are reducing agents (anti-oxidants) with the possible exception of iodine. Cuprous chloride alone has a catalytic effect, which may not be significant.

None of the inorganic compounds tried appreciably affected the rate of the Cannizzaro reaction of distilled aldehyde. None of them produced an air-vacuum difference.

TABLE 18

EFFECT OF ADDED INORGANIC SUBSTANCES ON
DISTILLED ALDEHYDE

Substance Added	Per Cent Reaction		Per Cent Reaction Nothing Added	
	Air	Vacuum	Air	Vacuum
1/10,000 pts. cupric nitrate	40	39	36	33
1/10,000 pts. cuprous chloride	32		35	33
1/10,000 pts. stannous chloride	33		35	33
0.1 gr. ferric chloride	17		19	
1/10,000 pts. silver nitrate	35		35	33
1/5,000 pts. chromic chloride	35		35	26
1/5,000 pts. lead nitrate	35		35	26
1/5,000 pts. sodium peroxide	34		21	
1/1000 pts. sodium nitrite	13		15	
1/1000 pts. sodium nitrite	12		15	
1/1000 pts. cuprous chloride				
0.5 cc. of 30% hydrogen peroxide	28		20	
1/1000 pts. sodium peroxide	25		26	

All the organic compounds tried which were found to affect the rate of the Cannizzaro reaction are inhibitors of the autoxidation of benzaldehyde. The results are listed in Table 19.

No substance in this table has an effect on aldehyde from the bottle when the reaction is carried out in vacuo, or when the aldehyde does not already show an air-vacuum difference. There was also no increase or decrease in rate with distilled aldehyde. Thus for any of the substances to have an effect on the rate of reaction, it is necessary that the unknown catalyst and oxygen be present together.

All of the catalysts are capable of peroxide formation. With the exception of catechol and hydroquinone, it is possible to correlate the effect on the rate of reaction with the ease of oxidation of the catalyst in alkaline solution. The inhibitors can form relatively stable oxides (of the amines for example) or stable final oxidation products (hydroquinone→quinone). This action of inhibitors is either the removal of the substance which absorbs oxygen or else the inhibitor itself absorbs the oxygen. Some such hypothesis is necessary since all the inhibitors decrease the rate of a reaction carried out in air, to that of a plain reaction in vacuo.

TABLE 19

EFFECT OF ADDED ORGANIC SUBSTANCES

Substance Added	Per Cent Reaction		Per Cent Reaction Nothing Added	
	Air	Vacuum	Air	Vacuum
Untreated Aldehyde				
0.5 gr. benzoic acid	13		15	
0.1 gr. benzoic acid	14		14	
0.1% ascaridole	33		50	
0.2% ascaridole	57		15	
0.1 gr. β -naphthol	57		15	
1/8880 pts. β -naphthol	70	30	34	36
1/5000 pts. β -naphthol	35	45	32	39
0.1 gr. phenol	59		15	
0.1 gr. acetone	12		15	
0.1 gr. methyl alcohol	44		15	
0.17 gr. ethyl alcohol	61		16	
0.1 gr. catechol	27		16	
0.1 gr. hydroquinone	40		91	44
0.2 gr. hydroquinone	43		72	
0.1 gr. tert. butyl alcohol	42		16	
0.26 gr. triphenyl carbinol	22		16	
0.1 gr. trichloroacetic acid	92		65	
0.001 moles salicylaldehyde	100		65	
1.0 cc. salicylaldehyde	60		80	51
0.1 gr. diphenylamine	38		91	44
0.1 gr. aniline	42	51	80	51
	40		91	44
Distilled aldehyde				
1/10,000 pts. phenyl propylene	37	34	37	32
1/10,000 pts. β -naphthol	33		35	33
1/10,000 pts. β -naphthol	35		35	33
1/5000 pts. methylene blue				
1/5000 pts. methylene blue	35		35	33
1/10,000 pts. hydroquinone	34		35	33
1/5000 pts. dibenzaldiperoxide	31	34	32	32
1/10,000 pts. quinone	33		35	33
1/5000 pts. dibenzoyl peroxide	36	37	32	32
1/5000 pts. hydrobenzoin	28	28	33	23
1/5000 pts. benzil	32	31	35	26
1/5000 pts. benzoin	31	31	35	26
1/5000 pts. perbenzoic acid	23	27	35	26
1/5000 pts. benzoic acid	27	26	25	23
1/5000 pts. m-nitro benzald.	24		26	
1% thiophenol	17		18	
0.12 gr. sodium benzoate	31	35	20	26
0.1 cc. phenylethyl alcohol	23		18	

*Calculated on the basis of the aldehyde.

SUMMARY OF RESULTS

In a preliminary study of the conditions for carrying out the Cannizzaro reaction with benzaldehyde in the presence of aqueous potassium hydroxide the following facts were noted.

1. The concentration of the alkali had a marked effect on the rate of reaction.

2. Although the reaction was carried out at only three temperatures, the temperature coefficient appeared to be low.

3. Changes in the ratio of the volume of the reaction vessel to the volume of the reaction mixture had a greater effect on the reaction rate of untreated than distilled aldehyde.

4. A standard set of conditions was adopted which consisted of using reaction vessels of the same size (bomb tubes of 18-20 cc. capacity), a reaction mixture composed of 5 cc. 50% KOH, 5 cc. of benzaldehyde (at room temperature) to which other substances were added only in catalytic quantities, and rotating the tubes containing the reaction mixtures in a thermostat for one hour at $25^{\circ} \pm 0.1^{\circ} \text{C}$.

Effect of Air on Benzaldehyde

1. With certain lots of untreated benzaldehyde a marked increase in the rate of reaction was noted when the reaction was carried out in the presence of air. In some of these instances the per cent disproportionation in the presence of air was more than twice that obtained for an identical sample in an evacuated tube. Only a few lots of benzaldehyde have shown this air-vacuum difference. It has not been possible to produce this effect with untreated benzaldehyde at will or to produce it at all with the distilled aldehyde. The magnitude of the air-vacuum difference was found to be related to the length of time which had elapsed since the container had last been opened.

2. Distilled benzaldehyde on standing, when stored in an evacuated vessel, was not found to undergo significant changes in rate of disproportion. On the other hand, distilled aldehyde stored in air showed a gradual increase in rate but never displayed an air-vacuum difference.

3. It is perhaps significant that distilled benzaldehyde suffered oxidation by air on standing much more readily than untreated aldehyde.

Effect of Light on Benzaldehyde

1. Distilled benzaldehyde exposed to sunlight or the light of a quartz mercury arc showed an increase in rate of Cannizzaro reaction. This increased rate gradually diminished on standing (a matter of days) to that of the non-illuminated material. A yellow color developed in benzaldehyde as a result of illumination which readily disappeared in the presence of air.

2. It is very interesting to note that by shaking distilled benzaldehyde in air after illumination the rate of reaction was greatly increased over that which was not shaken. It is this fact that seems to link together the effects of air and light.

3. Illuminated benzaldehyde containing a catalytic quantity of β -naphthol (added either before or after the illumination) showed a greater rate of disproportionation than plain illuminated benzaldehyde.

Effect of Added Substances

Of a great many inorganic and organic materials which were added to benzaldehyde only sulfuric acid, phosphorus pentoxide, and benzyl alcohol produced marked increase in rate of the Cannizzaro reaction.

EXPERIMENTAL PART

Method of Carrying Out the Reaction

All of the reactions, unless otherwise indicated, were carried out in pyrex reaction tubes having an outside diameter of 22 mm. and a total volume of 18-20 cc. 6 mm. pyrex tubes were sealed on at one end through which the reagents were added.

Five cubic centimeters of aqueous 50 per cent potassium hydroxide solution¹ was pipetted into each tube and then 5.0 cc. of benzaldehyde added in the same manner. Small pyrex glass funnels with long stems were used to introduce the alkali and aldehyde, a different funnel being used for each. When foreign materials were used, they were washed into the reaction tube with the aldehyde.

The reactions in air were made by sealing off the small tube, care being taken to remove all aldehyde and alkali from the seal.

When a reaction was carried out both in air and in vacuo, the potassium hydroxide solution was first solidified by cooling in a carbon dioxide-acetone bath, and the aldehyde then added. The air reactions were sealed off as before. The vacuum reaction tubes were evacuated with an oil pump while the tube was immersed in the cooling bath. This prevented the loss of both water and aldehyde. The tubes were then sealed off in vacuo. The reaction mixtures were warmed to 20-25° C. with water before shaking.

All reaction mixtures, whether in air or in vacuum, were agitated by rotating 58-60 times per minute, in a thermostat maintained at $25 \pm 0.1^\circ$ C. The time of shaking was one hour. At the end of this time, the tubes were removed and immediately placed in a carbon dioxide-acetone bath to prevent further reaction.

¹Baker and Adamson, Reagent Quality, potassium hydroxide sticks were used. A solution of the desired concentration was made up and standardized by titration using both phenolphthalein and methyl orange as indicators in order to correct for the presence of carbonates. The solution was stored in a paraffined bottle.

Method on Analysis

The reaction mixtures were analysed two at a time to prevent excessive atmospheric oxidation. Each tube was opened while cold and the contents washed with distilled water into a flask. The mixture was then transferred to a separatory funnel, the flask rinsed with water and then with 15 cc. of ether. This ether was used for the first extraction. A second portion of 15 cc. was used for the second extraction. It was assumed then, that all the unreacted benzaldehyde and all the benzyl alcohol were removed. The ether solution was evaporated, in weighed flasks, on a steam bath, and then the water removed by heating on a hot plate. When cool, the flasks were again weighed and the total weight of aldehyde plus alcohol determined.

The alkaline water solution from the extractions was acidified with concentrated hydrochloric acid and the solution cooled. The benzoic acid was then extracted with ether as before. The ether was evaporated off on a steam bath and the acid dried in a vacuum desiccator. The acid was then weighed.

This method of analysis was used with known mixtures of benzoic acid and benzyl alcohol and found to give almost quantitative recovery. The drying of the extracts was found to be the main source of error in the analysis.

To calculate the per cent Cannizzaro reaction, the weight of the aldehyde plus alcohol and of the acid was totaled, and this taken as the total weight of aldehyde used. This usually checked well with the actual weight of 5.0 cc. of benzaldehyde at room temperature. From the amount of acid formed in the reaction and the total weight, the per cent Cannizzaro reaction was calculated. A variation of $\pm 5\%$ or less in the per cent reaction is considered a check, although checks on identical reactions could be usually obtained within $\pm 2\%$.

Methods of Purification of the Aldehyde

At the beginning of this work, attempts were made to obtain peroxide-free benzaldehyde. To do this, the aldehyde was washed twice with saturated sodium sulfite solution, once with water, and then dried over anhydrous sodium sulfate. As soon as the aldehyde became clear, it was transferred to a flask containing hydrated ferrous sulfate, sealed to a vacuum line. The system

was evacuated and three successive distillations made from ferrous sulfate. In each distillation, the first fraction was discarded. A peroxide test with potassium thiocyanate and ferrous ammonium sulfate was carried out in the line. In all cases this test was positive. All such tests were considered reliable only if, upon opening the test tube, a dark red color immediately appeared on the surface of the solution.

It was found that sodium sulfite could not be used in the line as a scrubbing agent for the aldehyde, because an appreciable amount of sulfur dioxide could be detected in the final distillate.

Later experiments showed that one distillation without preliminary washing was as effective in purification as the more complicated procedure used previously. In all cases distillation was carried out in as diffuse light as possible. Care was taken to pump off all water and dissolved oxygen prior to distilling the aldehyde. Only the middle fraction was used.

Distillation of the aldehyde at reduced pressure in an atmosphere of carbon dioxide was carried out in a Claisen flask with a long neck which acted as a fractionating column. A very slow steady stream of carbon dioxide was pulled through the apparatus before and during the distillation. Again only the middle fraction was used.

Method of Illumination

Illumination of the aldehyde was carried out in pyrex glass tubes using a quartz mercury arc as a source of light. The tubes were placed in a motor driven rack which revolved about the arc three and one-half inches away. The time of illumination was one hour.

Titration of Peroxides

The method of Yule and Wilson¹ was used. Two cubic centimeters of benzaldehyde was added to 10.0 cc. of the ferrous sulfate, ammonium thiocyanate solution and the ferric ion formed, titrated with standard thallous chloride solution. All solutions were stored under an atmosphere of carbon dioxide. Blanks were run on the test solution if it was colored.

¹Yule and Wilson, Ind. Eng. Chem., 23, 1254-9 (1931).

Preparation of Peroxide-free Benzyl Alcohol

The benzyl alcohol was washed with saturated sodium sulfate solution, then with water, and dried over anhydrous sodium sulfate. It was distilled under reduced pressure in an atmosphere of carbon dioxide. A peroxide test made on the middle fraction was negative.

Action of Concentrated Sulfuric Acid on Benzaldehyde

When benzaldehyde was treated with concentrated sulfuric acid, a deep red solution formed. This was washed with water, ether added, and the mixture washed with dilute sodium carbonate solution. The ether solution was separated and added to a water solution containing an excess of sodium bisulfite. The mixture was shaken and allowed to stand until the reaction was complete. The bisulfite compound was filtered off and washed with water and ether. The ether in the filtrate was separated from the water solution and evaporated on a steam bath. Two different residues were obtained depending upon the original reaction conditions.

If a large quantity of sulfuric acid was added to the benzaldehyde and the solution treated as described above, washing with alkali caused the formation of an ether soluble compound which was dark green in color. When this was added to the sodium bisulfite solution the green color changed to yellow. The final residue was an amorphous, brown solid.

If only a small quantity (10 per cent by volume) of sulfuric acid was added to benzaldehyde and the solution treated as before, the final residue was a viscous oil, dark red in color. This was heated with alkaline 50 per cent alcohol water solution and the insoluble portion removed by filtration. When dry, this solid material was dark orange brown in color, soluble in ether and benzaldehyde, insoluble in acid. Treatment with concentrated hydrochloric acid gave a bright red solid. This solid, after drying, again formed the orange material which did not melt.

SUMMARY

1. The reactions of aromatic aldehydes with concentrated alkali have been divided into three classes.

2. A method has been proposed, of correlating the structure of aromatic aldehydes with each type of reaction.

3. A study of the Cannizzaro reaction of benzaldehyde has been made with respect to the conditions affecting the rate of reaction.

4. A difference in behavior has been observed between distilled aldehyde and ordinary aldehyde from a bottle. An "aging effect" of the aldehyde was studied.

5. Light, sulfuric acid, phosphorus pentoxide, and benzyl alcohol have been found to increase the rate of reaction of distilled aldehyde.

6. The effect, on the rate of reaction, of numerous inorganic and organic substances has also been studied.

